

EFFECTS OF SUPERCRITICAL SOLVENTS ON THE RATES OF HOMOGENEOUS CHEMICAL REACTIONS

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Discussion

A number of recent reviews describe supercritical fluid extraction (1,2,3), however, the literature contains relatively few examples where supercritical fluid solvents have been used to modify or control reaction rate constants. Liquid phase reactions have been studied over wide pressure ranges, e.g. 1-10 kbar, to determine activation volumes, i.e. the pressure derivative of the rate constant. These studies essentially ignore the highly compressible near supercritical region where activation volumes can become infinite, either positively or negatively.

It is ironic that the large growth in SF extraction at the Max Planck Institute in Germany in the 1960's was the result of a serendipitous discovery of the solvent power of supercritical ethylene during the "Aufbau" reaction of triethylaluminum with ethylene (4). The literature contains few examples where supercritical fluids have been used as a medium to modify or control reaction rate constants (5,6,7).

Simmons and Mason (7) observed an abrupt decrease in Δv^\ddagger near the critical conditions for the cyclic dimerization of C_2F_3Cl . It is due to the large negative partial molar volume of the dimer in the transition state. At 120°C, the rate constant doubled for a pressure increase from 43 to 53 bar. Paulaitis (6) measured activation volumes as low as -500 cc/mol for the Diels-Alder cycloaddition of isoprene and maleic anhydride in CO_2 . The rate constant increased about 60% for a change in pressure of several bar. The pronounced solvent effect is due to the large dipole moment of the transition state, which is on the order of 3-7 Debye for other dienes with maleic anhydride (8).

The objective is to measure and to predict the effects of supercritical fluid solvents on reaction rate constants. In the near critical region, all of the density dependent variables such as the dielectric constant, refractive index, fugacity coefficient, and solubility parameter are extremely strong functions of temperature and pressure. This sensitivity, which is used advantageously in supercritical fluid extraction, could also be exploited in reaction processes. For example, rate constants could be changed orders of magnitude using modest changes in the temperature and pressure in the critical region. A UV-visible spectroscopic technique has been applied to supercritical fluids for the first time to determine the solvent polarity as a function of temperature and pressure. Solvent polarity scales based on solvatochromism, i.e., shifts in the absorption wavelength of indicator dyes caused by the solvent, are used commonly to correlate and to predict rate constants for liquid phase reactions. Novel processes could be developed using supercritical fluid solvents to achieve and control the desired selectivity in parallel reactions, the yield in reversible reactions, and to recover and purify reaction products efficiently using supercritical fluid extraction.

Conclusions

For dyes such as phenol blue, solvatochromic shift data provide a sensitive indication of the structure and polarity of supercritical fluid solvents. The polarities of supercritical ethylene and liquid hexane become equivalent for a density ratio of C_2/C_6 of 2.7 since the latter is more polarizable. At 25°C and 66 bar, the data were used to predict that the activation volume is -5000 cc/mol for the Menshutkin reaction of tripropylamine and methyl iodide. This large negative value is due to the high compressibility of SF ethylene in the critical region. These results suggest that rate constants may be altered markedly in SF solvents using small changes in

temperature and pressure.

The theory of solvent effects on electronic spectra can be extended to the SF state by including the effects of the isothermal compressibility. The local density of the SF solvent about the solute can be obtained by comparing the experimental E_T with the intrinsic value, E_T^0 , which is calculated straightforwardly for incompressible liquids. At the bulk density, the polarity of the SF solvent is equivalent to that of a hypothetical reference liquid at the local density. The specific polarity, which is due to hydrogen bonding, may be obtained by comparing this hypothetical reference fluid with the experimental data. For CF_3H , the specific polarity appears to be less sensitive to density than the intrinsic polarity. The understanding of the polarity of SF solvents at the microscopic level will benefit the development of both extraction and reaction process at SF conditions.

References

1. Paulaitis, M.E.; Krukonis, V.J.; Kurnik, R.T.; Reid, R.C., Rev. in Chem. Engr., 1(2), 179-250 (1983).
2. Johnston, K.P., "Kirk-Othmer Encyclopedia of Chemical Technology," John Wiley and Sons, Inc., New York (1984).
3. MuHugh, M.A., "Extraction with Supercritical Fluids," in "Recent Developments in Separation Science," Li, N.N.; Carlo, J.M., Ed.; CRC Press, Inc.: Boca Raton, FL, vol. IX, 1984.
4. Zosel, K., Angew. Chem. Int. Ed. Engl., 17, 702 (1978).
5. Randall, L.G., Sep. Sci. Technol., 17, 1 (1982).
6. Alexander, G.; Paulaitis, M.E., AIChE Annual Meeting, #140 d, San Francisco (1984).
7. Simmons, G.M.; Mason, D.M., Chem. Eng. Sci., 27, 89 (1972).
8. Eckert, C.A.; Hsieh, C.K.; McCabe, J.R., AIChE J., 20(1), 20-36 (1974).